Spectroscopic Studies of Intracluster Chemistry

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ABSTRACT

Infrared predissociation spectroscopy of ion-solvent clusters has allowed us to examine the effects of sequential hydration on the reactivity of cations such as NO^+, NO_2^+, and protonated formaldehyde, H_2COH^+, stable gas phase ions which are known to undergo rapid reactions in aqueous solution. Our experiments demonstrate that these ions undergo hydration reactions at critical cluster sizes. The smaller clusters have spectra characteristic of H_2O ligands bound to stable ion cores, but as the cluster size increases, there is a sudden onset for intracluster rearrangements, e.g. $NO_2^+ + H_2O \rightarrow H_3O^+ + HNO_3$ which occurs upon hydration with four water molecules. With this approach, we can probe microscopic aspects of solvent effects on chemical reactions including the hydration of carbonyls and acid-catalyzed hydrolysis of amides.

1.INTRODUCTION

Studies of solvated cluster ions in the gas phase have proven to be a powerful probe to understand the fundamental ion-solvent interactions usually obscured by the intrinsic averaging in the bulk. Infrared predissociation spectroscopy in tandem with mass spectrometry has been successful in investigating weakly-bound cluster ions in the gas phase. Substantial information on cluster structure, dissociation dynamics, and intracluster rearrangement can be obtained by monitoring the vibrational photofragmentation patterns of a mass-selected solvated ion.[1] Here we describe our recent application of this technique to the hydrated clusters of nitrosonium (NO^+), nitronium (NO_2^+) and protonated formaldehyde (H_2COH^+) ions.

The nitrosonium ion NO^+ and its hydrates play an important role in the ion chemistry of Earth's upper atmosphere.[2] Gas-phase experiments have primarily explored the association kinetics and thermochemistry to explain the production of hydrated hydronium ion in the stratosphere.[3-6] Fehsenfeld *et al.*[4] proposed the hydration mechanism; $NO^+(H_2O)_3 + H_2O \rightarrow H_3O^+(H_2O)_2 + HONO$. Puckett *et al.*[5] and several other groups measured the rate constants and French *et al.*[6] obtained hydration enthalpies. Theoretical calculations have examined the optimized geometries of protonated nitrous acid. De Petris *et al.*[7] performed *ab initio* calculations and predicted that protonated nitrous acid has six different isomers which are true minima on the potential energy hypersurface. The most stable form is an ion-molecule complex between NO^+ and H_2O shown in Fig.1. The next lowest energy isomers are formed by protonating either the terminal oxygen to form $N(OH)_2^+$, or the nitrogen atom to form $HON(H)O^+$ isomers. Using collisionally-activated dissociation (CAD) mass spectrometry, De Petris *et al.* presented circumstantial evidence that this isomer is the complex $NO^+(H_2O)$. However, they observed no metastable signal and thus were unable to glean further structural information on protonated nitrous acid .

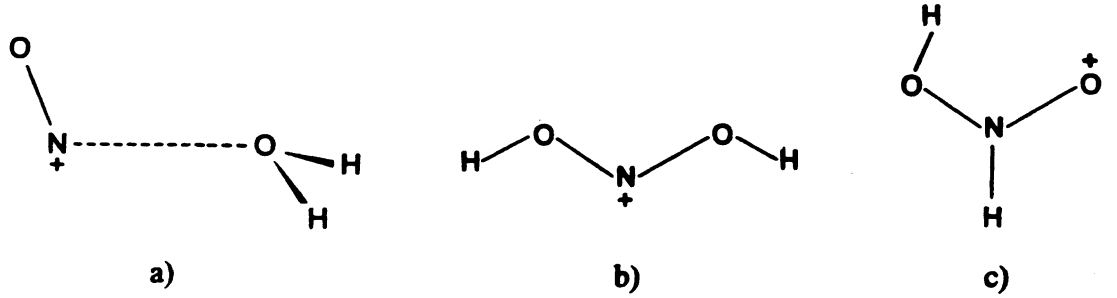

Fig. 1. Isomers of protonated nitrous acid. The geometry of the most stable structure predicted at the MP2/6-31G** level is a) $NO^+(H_2O)$, while b) $HONOH^+$ and c) $HON(H)O^+$ are potential energy minima lying at higher energies.

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The existence of the nitronium ion NO_2^+ and its hydrate was inferred by Fehsenfeld *et al.*,[8] who studied the ion chemistry of HNO_3 in a flowing afterglow apparatus. They observed rapid proton transfer from H_3O^+ to HNO_3, and attributed the decay of $H_2NO_3^+$ to its association with H_2O. However, they were unable to detect hydrated clusters of protonated nitric acid, and postulated a fast reaction $NO_2^+(H_2O)_2 + H_2O \rightarrow H_3O^+(H_2O) + HNO_3$ that would destroy the association products and convert NO_2^+ to HNO_3. Theoretical studies[9,10] have shown that gas phase protonated nitric acid $H_2NO_3^+$ possesses several isomers. The most stable form is a weakly-bound complex of NO_2^+ and H_2O. Cacace *et al.*[11] found experimental evidence for a second isomer, $(HO)_2NO^+$, which lies 10-20 kcal/mol higher. *Ab initio* calculations by Lee and Rice[10] confirmed the structures and relative stability of the two isomers, but the computed proton affinity for nitric acid is 182 ± 4 kcal/mol, in disagreement with Cacace's ICR bracketing measurement of 168±3 kcal/mol and closer to an earlier measurement of 176±7 kcal/mol.

Protonated formaldehyde, CH_2OH^+, and its hydrate clusters are important species known to exist in the stratosphere. Gas-phase experiments[12-14] demonstrated that hydrated formaldehyde clusters react with H_2O to form $H_3O^+$and CH_2O for small n and that the reactions proceed quite fast, typically $k \approx 2\times 10^{-9}$ cm^3 s^{-1}. However, those reactions had quite small reaction enthalpies and recent theoretical calculations[15] on the hydration reaction of neutral formaldehyde predicted the possibility of forming thermodynamically more stable 1.1 diol. Although the high activation barrier in neutral CH_2O hydration reaction prevents substantial formation of 1.1 diol, the hydration of protonated formaldehyde through favorable ion-solvent interaction might lower the barrier significantly, resulting in the formation of diol at high n. Existence of 1.1 diol is quite well characterized in aqueous solution, but the structures of $H_3O^+(CH_2O)(H_2O)_n$ and their reaction mechanism are not known.

In this manuscript, we describe our investigations of the vibrational predissociation spectroscopy of $NO^+(H_2O)_n$, and $NO_2^+(H_2O)_n$ and preliminary results of $H_2CO^+(H_2O)_n$ clusters. We have also performed *ab initio* calculations of the vibrational frequencies and intensities of the clusters $NO^+(H_2O)_n$ (n= 1 and 2) to confirm our vibrational assignments. Our calculations were undertaken because there were no published theoretical estimates of the vibrational frequencies for n = 1 nor of the structure, energetics, and vibrational frequencies for n = 2.

2.EXPERIMENTAL

The apparatus employed in these experiments has been described elsewhere,[16,17] and is briefly described here. For $NO^+(H_2O)_n$ (n = 1 to 5) clusters, an MKS mass-flow controller was used to produce a mixture of 12% NO seeded with water vapor in UHP H_2 or He at room temperature. To generate $NO_2^+(H_2O)_n$ (n = 1 to 5) clusters, UHP He was seeded with HNO_3/H_2O vapor by passage over the surface of nitric acid (70%) at O°C. In $H_2COH^+(H_2O)_n$ (n = 1 to 6) clusters, UHP H_2 was mixed at -77°C with the purified liquid formaldehyde obtained by vacuum distillation of paraformaldehyde. The gas mixture at a total stagnation pressure of 1000 Torr expanded through a piezo-driven pulsed valve into a 1 mm diameter, 1.5 cm long channel where a high voltage pulse (1.5–3 kV, 100 μs wide) was applied between two electrodes. The ions formed in the plasma were thermalized as the gas flowed through the channel and further cooled in the supersonic expansion into the first differential vacuum chamber maintained at 2 to 5 $\times 10^{-5}$ Torr by a 10 in. diffusion pump. The expanding ions were skimmed and entered a second region (6 in. diffusion pump, 1×10^{-6} Torr) containing the time-of-flight ion optics. The ions were extracted by a pulsed electric field 15 μs in duration and accelerated to 1.3 kV, focused by a pair of einzel lenses. The ions passed through an additional stage of differential pumping (4 in. diffusion pump, 1×10^{-6} Torr) and entered the photolysis chamber (500 L/s turbomolecular pump, 3×10^{-7} Torr).

Parent ions of a specific mass were selected by a 1 cm long mass gate which rejected all ions of other *m/e*. The ions were vibrationally excited by a collimated tunable infrared beam, which was generated by a pulsed $LiNbO_3$ optical parametric oscillator (OPO)[18] and timed to intersect the selected ions at the spatial focus of the time-of-flight mass spectrometer. The OPO was pumped by a Nd:YAG laser and was tunable from 2700 to 6700 cm^{-1} by simultaneously adjusting the crystal and grating angles. Typical OPO pulse energies were about 3 to 7 mJ with a line width of 1.5 cm^{-1}. The resulting photofragment ions through vibrational predissociation were separated in time from

the parent ions using a reflectron energy-analyzer, and then detected by a microchannel plate detector. The signal was preamplified and then collected by a transient digitizer.

Predissociation spectra were obtained by stepping the OPO wavelength and averaging the photofragment ion signal for 200 shots at each wavelength. Fragment ion background arising from dissociation of metastable parents was subtracted to obtain the fragment signal due solely to photodissociation. The data were then normalized with respect to the OPO pulse energy. Between 2 and 14 such scans were averaged, depending on the photofragment signal intensity. The OPO laser wavelength was calibrated during the scan by simultaneously recording the fundamental and overtone spectra of either methane or hydrogen chloride in a photoacoustic cell.

4. RESULTS AND DISCUSSION

4.1. $NO^+(H_2O)_n$ Clusters

We recorded infrared spectra of mass-selected clusters $NO^+(H_2O)_n$ for n=1-5 in the 2700-3800 cm^{-1} region. Fig.2 presents the infrared spectra for n=1-5 over the entire frequency range.

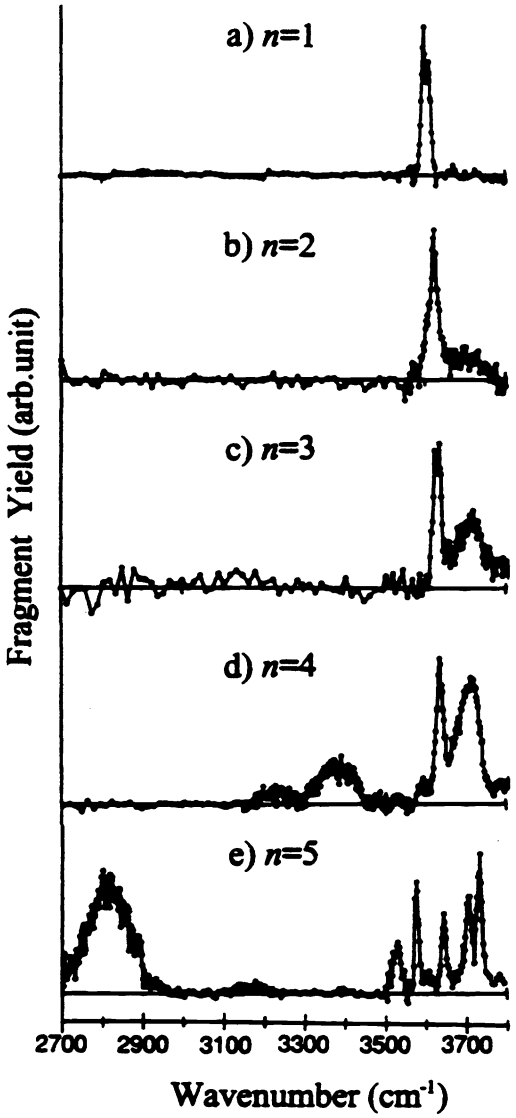

Fig. 2. Vibrational predissociation spectra of $NO^+(H_2O)_n$ (n = 1–5). The photofragment ions detected were $NO^+(H_2O)_{n-1}$ (n = 1–4) and $H_3O^+(H_2O)_3$ (n = 5), respectively.

The only photofragment ions detected in n=1 were NO^+. The fragment signal exhibited a quadratic dependence, indicating that two photon excitation was involved. The infrared spectrum (Fig.2a) exhibited a single vibrational band. This band was only 50 cm^{-1} lower in frequency than the symmetric stretch of the water monomer and a doublet with maxima at 3599 and 3611 cm^{-1}. The experimental results are most consistent with the structure of a weakly bound ion-molecule complex, $NO^+(H_2O)$. We could not find any evidence for the higher energy isomers predicted to have strong bands below 3500 cm^{-1}. The frequency of the observed vibrational band, 3605 cm^{-1}, agrees within 5% of the scaled MP2 frequency of the H_2O symmetric stretch, 3587 cm^{-1}. We do not observe an antisymmetric stretch band, which our calculations predict would occur at 3671 cm^{-1} (scaled) with an intensity 80% of that of the symmetric stretch. The reason for the absence may lie in the fact that the spectra are not absorption spectra, but rather two-photon dissociation spectra.

The only process observed for n=2 and n=3 was a single water molecule evaporation: $NO^+(H_2O)_n \rightarrow NO^+(H_2O)_{n-1} + H_2O$, n = 2,3. In the case of n = 2, the fragment ion signal showed both linear and nonlinear behavior depending on source conditions. The detected signal for n = 3 depended linearly on laser power, indicating that the predissociation of this cluster was a single photon process. Unlike the n = 1 cluster, these clusters had two absorption bands (Fig.2). The lower frequency bands at ca.3630 cm^{-1} were sharp and resembled in shape and position the band observed for $NO^+(H_2O)$. The higher frequency bands at ca. 3700 cm^{-1} were broad. We assigned these bands to the symmetric and antisymmetric stretch modes of water ligands, respectively. The similarity in the spectra and photoproducts of n = 1 and its hydrates (n = 2,3) suggest that these clusters also have water ligands bound to an NO^+ ion core. This inference is confirmed by the fluence dependence, the smaller red-shifted band positions of the water stretches and the *ab initio* structures in which the water ligands bind to the nitrogen atom of the NO^+, as in n = 1.

Infrared excitation of the n = 4 cluster produced photofragments at three masses, corresponding to $NO^+(H_2O)_3$, $NO^+(H_2O)_2$, and $H^+(H_2O)_3$. The major dissociation channel was loss of one water. The $NO^+(H_2O)_2$ product could be either from spontaneous dissociation of the primary product, $NO^+(H_2O)_3$ or more likely from the evaporation of a neutral water dimer $(H_2O)_2$, a process which requires less energy. The observation of $H^+(H_2O)_3$ signaled the onset of a new dissociation channel, loss of a nitrous acid molecule. The relative yields were wavelength dependent. In the 3600-3800 cm^{-1} region, the branching ratio of three channels was 8 : 1.5 : 1. The water-loss channel was predominant when exciting bands in the 3400 cm^{-1} region. The spectrum consisted of four bands (Fig.2d). Two bands at 3635 and 3713 cm^{-1} were similar to the bands observed in $n \leq 3$, and two new bands at 3230 and 3375 cm^{-1} were substantially broader. The two high frequency bands were assigned to H_2O symmetric and antisymmetric stretches, respectively. The two lower frequency bands were broad and significantly red-shifted relative to the other OH bands, indicative of an OH bond involved as a donor in hydrogen bonding.

The simplest configuration involves the fourth water forming a hydrogen bond with one of the first shell H_2O molecules. However, this configuration will give rise to only one hydrogen-bonded OH absorption band. The most plausible geometry is a bridging structure (Fig.3a). Small water clusters are well known for forming cyclic structures in order to maximize stabilization by hydrogen bonding.[19] If the water bridges two adjacent ligands to form a ring of four heavy atoms (three water O atoms and the N^+), then the $H_2O\cdots N\cdots OH_2$ angle is 120° and the N···O bond length is 2.4 Å (slightly longer than calculated for n=2). The separation between O atoms on the H_2O ligands is 4.2 Å, comparable to the 4.48 Å distance in ice. This structure is similar to tetrahedral structures existing in ice VI. By forming two hydrogen bonds, the second shell H_2O should bind by at least 12 kcal mol^{-1}; even with some reduction stemming from ring strain. The bands observed at 3230 and 3375 cm^{-1} could then be assigned as symmetric and antisymmetric stretch modes of the two hydrogen-bonded OH bonds. Another probable geometry is one proposed by Fehsenfeld *et al.*[4] as an intermediate in the reaction from $NO^+(H_2O)_2 + H_2O$ to $H_3O^+(H_2O)_2 + HONO$ (Fig. 3b and 3c). The structure has one (first shell) H_2O bound to NO^+, with a single H_2O in turn bound to that. The remaining two H_2O molecules were in the third shell, hydrogen-bonded to the second shell H_2O. This structure is consistent with our observed spectrum, since there are three hydrogen-bonded OH groups, as well as two H_2O ligands with free OH groups. If the charge remains localized on the N atom, however, this configuration will be highly energetic, and unlikely to be formed.

The observation of HONO products in the absence of an HONO absorption band suggests that one IR photon can induce the reaction $NO^+(H_2O)_4 \rightarrow H_3O^+(H_2O)_2$ + HONO. French *et al.*[6] estimate that the two channels, loss of H_2O and loss of HONO, are almost identical in energy, but we find that the yield of HONO is significantly lower (10%). There are several plausible reasons why unimolecular decay of excited $NO^+(H_2O)_4$ favors H_2O loss. First, the estimated dissociation energies are comparable to the photon energy; if the molecule is excited close to threshold, differences of even a few kcal mol^{-1} can greatly influence the branching ratio. Second, the reaction may have an activation energy significantly larger than the H_2O binding energy, E_{act} > 10 kcal/mol. A barrier between $NO^+(H_2O)_4$ and $H_3O^+(H_2O)_2$(HONO) is plausible, especially if the solvent H_2O must rearrange as the charge is transferred. Finally, unimolecular decay via the reactive channel may also be limited by the entropy of activation. Evaporation of H_2O from $NO^+(H_2O)_4$ proceeds by simple bond fission, but formation of HONO may occur by a concerted reaction requiring substantial rearrangement.

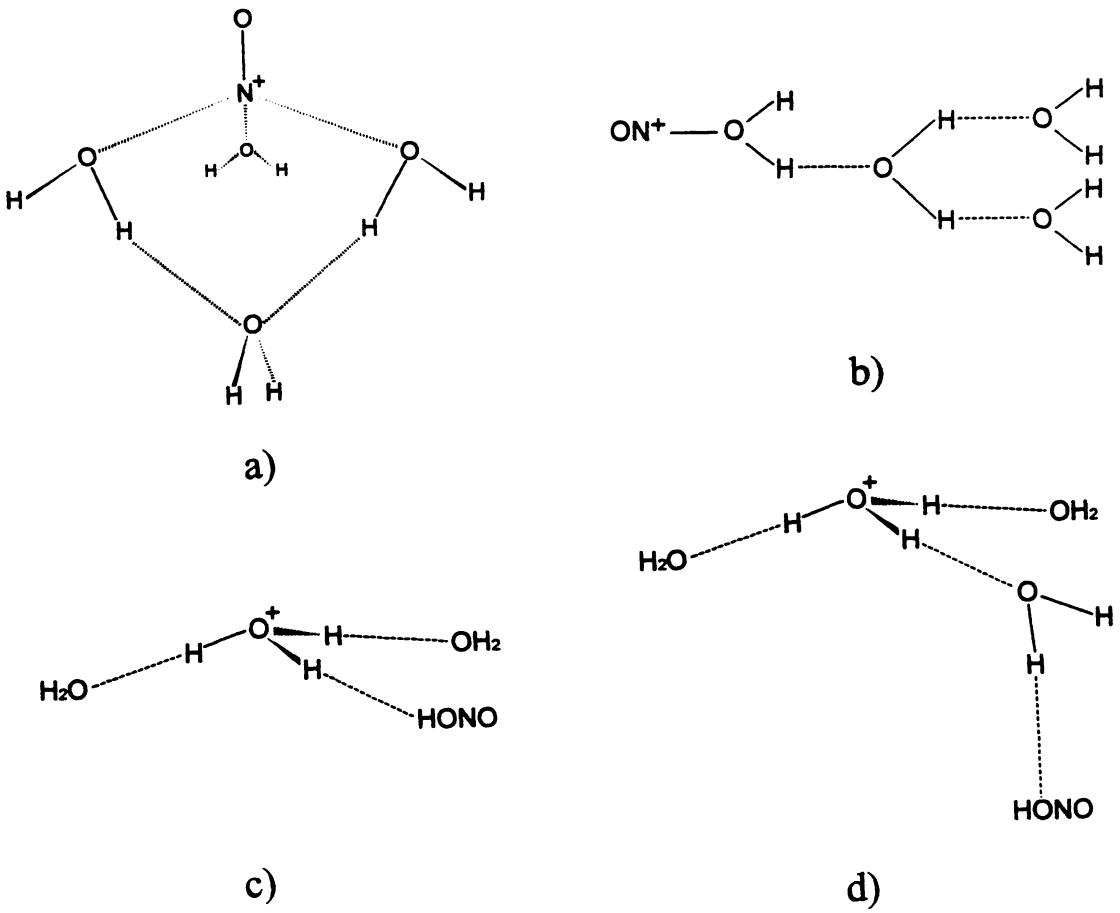

Fig. 3. Proposed structures of the nitrosonium ion hydrates $NO^+(H_2O)_n$, for n = 4 and 5.

There was a significant change in the photofragmentation pattern and spectrum in the n = 5 cluster, $NO^+(H_2O)_5$. We detected photofragments at three masses: $H^+(H_2O)_4$, $H^+(H_2O)_3$, and $NO^+(H_2O)_4$. The dominant channel throughout the observed spectral region was $NO^+(H_2O)_5 \rightarrow H_3O^+(H_2O)_3$ + HONO. The infrared absorption spectrum possessed seven distinct bands, two in the 2700-3200 cm^{-1} region, and five others in the 3500-3800 cm^{-1} region (Fig.2e). We assigned the strong and broad band at 2800 cm^{-1} to the hydrogen-bonded OH antisymmetric stretch of the H_3O^+ ion and the weaker 3190 cm^{-1} band to the companion mode. The five higher frequency bands can

be assigned as OH stretches of the ligands bound to the H_3O^+ core. Since HONO is the dominant dissociation product, we infer that HONO forms weaker hydrogen bonds than H_2O. We thus propose that the n = 5 clusters have the structure with the H_3O^+ bound to three water molecules in the first solvation shell and a HONO molecule in the second shell hydrogen-bonded to one of the first shell waters (Fig.3d). Given this structure, we can assign the five bands. The bands at 3644 and 3734 cm^{-1} are assigned as the symmetric and antisymmetric OH stretches of the two water ligands (not bound to HONO). We assign the 3710 cm^{-1} band to the free OH of the HONO-bound water, and the broader band at 3530 cm^{-1} to the HO—H···O bond. The remaining band, the sharp, strong feature at 3576 cm^{-1}, is assigned to the OH stretch of the *trans* nitrous acid ligand.[20,21] The n = 5 cluster reflects the fact that the reaction $NO^+(H_2O)_4 + H_2O \rightarrow H_3O^+(H_2O)_3 +$ HONO is thermodynamically favored.

In summary, our results provide clear evidence for a rearrangement of $NO^+(H_2O)_n$ at larger cluster sizes. The experimental results indicate that the smaller clusters are nitrosonium ions bound by water ligands and are in accord with the theoretical calculations for n = 1 and 2. The cluster n = 4, however, begins to deviate from this picture with the appearance of new hydrogen-bonded OH stretch absorptions and the opening of a minor photodissociation channel giving rise to loss of HONO. This behavior presages the large changes in the vibrational spectrum and photodissociation behavior observed upon adding a fifth water molecule. The n = 5 cluster forms an adduct of the reaction products, $H_3O^+(H_2O)_3$(HONO).

4.2. $NO_2^+(H_2O)_n$ Clusters

The only predissociation process observed in n=1 was: $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$. The dissociation signal was very weak and exhibited a nonlinear dependence on laser intensity, indicating that the photodissociation arose from a multiphoton process. The infrared spectrum had two distinct bands, one centered at 3626 cm^{-1} and the other a doublet with maxima at 3708 cm^{-1} and 3716 cm^{-1}. These were red-shifted by less than 50 cm^{-1} from the symmetric and antisymmetric stretching bands of the water monomer. Coupled with the absence of bands near 3550 cm^{-1}, we conclude that protonated nitric acid is a weakly-bound complex $NO_2^+(H_2O)$, in agreement with earlier studies. This is consistent with the structure calculated by Lee and Rice[10], a highly asymmetric top for which the symmetric H_2O stretching mode would be an *a* type band and the antisymmetric mode a *b* type band. We found no evidence for the formation of the higher energy isomer $(HO)_2NO^+$ or its hydrates in our source. While this ion is covalently bound and may not predissociate upon photon absorption, the hydrates should. MP2 calculations[10] predict that the (scaled) NO-H stretching frequencies lie near 3450 cm^{-1}, but no such bands were observed in any clusters.

Clusters of protonated nitric acid solvated by one or two water molecules, $NO_2^+(H_2O)_n$ (n=2,3), showed a single water molecule evaporation: $NO_2^+(H_2O)_n \rightarrow NO_2^+(H_2O)_{n-1} + H_2O$. In both clusters, only two bands were observed in the OH stretch region, slightly red-shifted from the water symmetric and antisymmetric stretches, respectively. The dissociation signal was much stronger than for n = 1 and depended linearly on laser intensity. The similarity in the spectra and the photoproducts of n=1 and its hydrated clusters (n=2,3) indicates that the smaller hydrates are also complexes of an NO_2^+ ion core and H_2O ligands (Fig. 4a). With additional ligands, the binding energy should be lower and the H_2O stretching modes less perturbed. This inference is confirmed by the stronger signal and its linear power dependence, as well as the smaller red-shift of the H_2O bands.

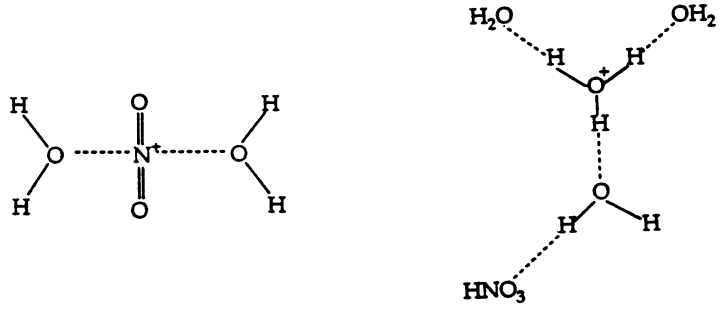

Fig. 4 The proposed structures for $NO_2^+(H_2O)_2$ and $NO_2^+(H_2O)_5$.

For clusters $NO_2^+(H_2O)_n$ with $n \geq 3$, we observed the onset of a new photodissociation channel, loss of a nitric acid molecule, $NO_2^+(H_2O)_n \rightarrow NO_2^+(H_2O)_{n-1} + HNO_3$ in competition with the water loss channel. Although evaporation of nitric acid was a minor channel for $n = 3$ predissociation, it was a major channel for $n = 4$ and the dominant channel for $n = 5$. The ratio of the nitric acid channel yield to the water channel yield was 1:8 for $n = 3$, and 9:1 for $n = 5$. In $n = 4$, the yield depended on the band excited: it was 7:1 upon excitation in the 3550 cm^{-1} region and 2:1 in the 3600-3800 cm^{-1} region. Three new bands were observed for the clusters $NO_2^+(H_2O)_4$ and $NO_2^+(H_2O)_5$ in addition to the two H_2O bands (Fig. 5). The broad band at 2600-2700 cm^{-1} was assigned to the hydrogen-bonded OH stretches of the H_3O^+ ion core. The appearance of nitric acid-like bands near 3550 cm^{-1} and the onset of dissociation releasing HNO_3 indicate that neutral HNO_3 exists in the clusters. We therefore conclude that the larger clusters $n \geq 5$ are complexes of an H_3O^+ core surrounded by water ligands and a neutral HNO_3 (Fig. 4b). The wavelength dependence of the branching ratio in the $n = 4$ cluster suggests that two nearly isoenergetic isomers are present, one with a hydronium ion core, $H_3O^+(H_2O)_2(HNO_3)$, and the other with a nitronium ion, $NO_2^+(H_2O)_4$.

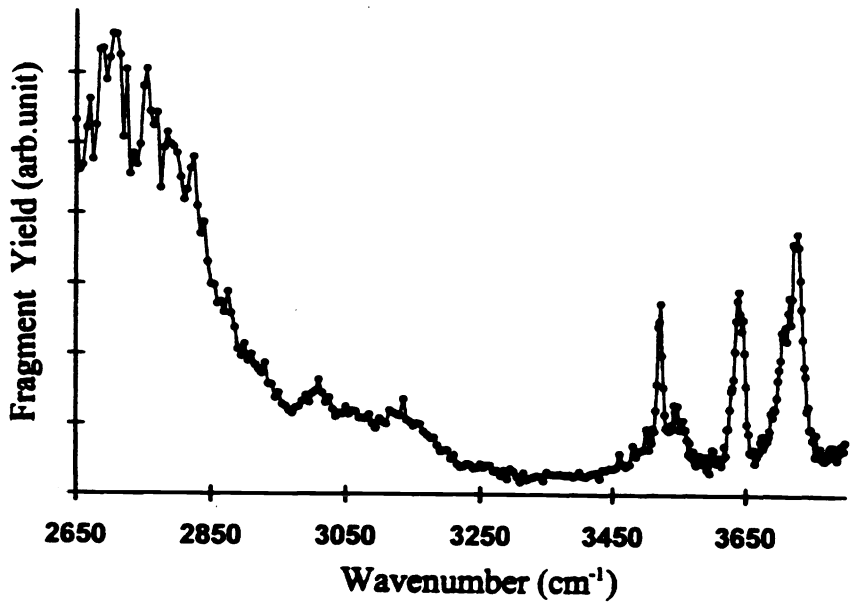

Fig. 5 Infrared predissociation spectrum of $NO_2^+(H_2O)_5$. The ordinate is the $H_3O^+(H_2O)_3$ photofragment signal.

In summary, infrared spectra of clusters of protonated nitric acid and water shows that in small clusters, water binds to a nitronium ion core, but at a critical cluster size the NO_2^+ reacts; $NO_2^+ + 2H_2O \rightarrow HNO_3 + H_3O^+$ The driving force for overcoming the intrinsic stability of gas phase NO_2^+ is the solvent stabilization of H_3O^+.

4.3. $H_3O^+(CH_2O)(H_2O)_n$ Clusters

Protonated formaldehyde water clusters, $H_3O^+(CH_2O)(H_2O)_n$ are being investigated, and here we present some preliminary results. For n=4, we observed two photoproducts, $H_3O^+(CH_2O)(H_2O)_3$ and $H_3O^+(H_2O)_4$. The major photodissociation process was a single water evaporation: $H_3O^+(CH_2O)(H_2O)_4 \rightarrow H_3O^+(CH_2O)(H_2O)_3 + H_2O$. This cluster had four absorption bands in the 2800-3800 cm^{-1} region. The band at ca.3645 cm^{-1} is assigned to the symmetric stretch of water ligands and two bands at ca. 3700 and 3735 cm^{-1} to the antisymmetric stretches of water ligands. The band at ca. 3200 cm^{-1} was broad and significantly red-shifted relative to the other OH bands, indicative of an H-bonded OH stretch. However, we did not find any evidence for C-H stretches of diols. The reason might be the negligible absorption cross section of the C-H stretch. Other larger clusters are being studied to elucidate the mechanisms and structures.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. *Ion and Cluster Ion Spectroscopy and Structure*, edited by J. P. Maier (Elsevier, Amsterdam,1989).
2. E. E. Ferguson, F. Fehsenfeld, and D. L. Albritton, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers, Academic Press, New York (1979); G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, D. Reidel, Dordrecht, Holland (1986).
3. R. S Narcisi and A. D.Bailey, J. Geophys. Res. **70**, 3687 (1965).
4. F. C. Fehsenfeld and E. E. Ferguson, J. Geophys. Res. **74**, 2217 (1969).
5. W. C. Lineberger and L. J. Puckett, Phys. Rev, **187**, 286 (1969)
6. M. A. French, L. P. Hills and P. Kebarle, Can. J. Chem. **51**, 456 (1973).
7. G. De Petris, A. D. Marzio and F. Grandinetti. J. Phys. Chem. **95**, 9782 (1991).
8. F. C. Fehsenfeld, C. J. Howard and A. L. Schmeltekopf, J. Chem. Phys. **63**, 2835 (1975).
9. M.-T. Nguyen and A. F. Hegarty, J. Chem. Soc. Perkin Trans. II, 2043 (1984).
10. T. J. Lee and J. E. Rice, J. Phys. Chem. **96**, 650 (1992); J. Am. Chem. Soc. **114**, 8247 (1992).
11. F. Cacace, M. Attina, G. de Petris and M. Speranza, J. Am. Chem. Soc. **111**, 5481 (1989); J. Am. Chem. Soc. **112**, 1014 (1990).
12. F. C. Fehsenfeld, I. Dotan, D. L..Albritton, C. J. Howard, and E. E. Ferguson, J. Geophys. Res. **83**, 1333 (1978).
13. M. Meot-Ner, J. Am. Chem. Soc. **106**. 1265 (1984).
14. D. Wayne Berman and J. L. Beauchamp, J. Phys. Chem. **84**. 2233 (1980).
15. B. C. Garrett and C. F. Melius, Theoretical and Computational Models for Organic Chemistry. S. J. Formosinho *et al.* (eds.), Kluwer Academic Publisher. Printed in the Netherlands.
16. Y. Cao, J. -H. Choi, B. -M. Haas, M. S. Johnson and M. Okumura, J. Chem. Phys. **99**, 9307 (1993).
17. Y. Cao, J. -H. Choi, B. -M. Haas, M. S. Johnson and M. Okumura, J. Phys. Chem. **97**, 5215 (1993).
18. S. J. Brosnan and R. L. Byer, IEEE J. Quantum Electronics **QE-15**, 415 (1979).
19. See for example S. S. Xantheas and T. H. Dunning, J. Chem. Phys. **99**, 8774 (1993).
20. S. M. Holland, R. J. Stickland, M. N. R. Ashfold, D. Z. Newnham and I. M. Mills. J. Chem. Soc., Faraday Trans. , **87**, 3461 (1991).
21. C. M. Deeley and I. M. Mills. J. Mol. Struct., **100**, 199 (1983).